POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #4

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The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

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1 Summary

Electrochemical characterization is nearly complete. The data so far indicates that the Ni/Zn alloys do provide cathodic protection to steel despite having a lower than expected concentration of Zn. PPG demonstrated successful scale-up to 120 g batches, the ability to spray paint test panels without evidence of premature microcapsule rupture, and have shown that the microcapsules are resilient to solvent soaking.

2 Project Goals and Objectives

This month marks the milestone in which the most suitable Ni/Zn alloy composition was supposed to be chosen based on its galvanic protection capability. Electrochemical characterization suggests that all Ni/Zn alloys achieve the requisite -100 mV polarization for cathodic protection. However, the degree of cathodic protection does not currently appear to vary with Zn concentration. Unless future measurements demonstrate a clear correlation between Zn concentration and cathodic protection, then an optimum composition will be chosen based on cost and processability instead. The next major milestone is the ability to heal 1/32" scratches by the end of next month. A milestone that was originally slated for month 9–successful spray painting of test panels–has already been reached.

3 Key Accomplishments

3.1 Electrochemical Characterization

In order to quantify the cathodic protection capability of Polyfibroblast microcapsules, we designed the following test. We short-circuited a A1008 steel specimen to a strip of polyurethane containing Polyfibroblast, and then immersed the two in an aerated aqueous solution of sodium chloride. If steel was not shorted to Polyfibroblast, we observed rapid corrosion. In order to verify the cathodic protection (CP) capability of the Polyfibroblast, we measured the electrochemical potential of the steel and the short circuit current between the steel and the Polyfibroblast strip. The short-circuit current, which is identical to the cathodic protection current, was measured using the Zero-Resistance-Ammeter (ZRA) provision in the Solartron Electrochemical Interface (potentiostat/galvanostat) Model SI 1287; the same instrument also supports electrochemical potential measurements.

Note that the steel test specimen was an annealed strip of A1008 steel. The polyurethane containing Polyfibroblast strip was applied to a conducting surface in order to ensure electrical contact. A Calomel electrode (Hg/HgCl/0.1 M NaCl) was used as the reference electrode. The test solution was 0.1 M NaCl; air was constantly bubbled through the solution to maintain a constant concentration of dissolved oxygen. The A1008 steel and polyurethane-Polyfibroblast strip containing 5% Zn were kept in an empty beaker and shorted through the ZRA. Next, the aerated 0.1 M NaCl was introduced into the beaker. Thus, the A1008 steel was under cathodic protection by the polyurethane-Polyfibroblast strip even before making contact with the salt solution. The potential and the current measurements were started immediately. The results are shown in Figure 1 for polyurethane-Polyfibroblast strip containing various amounts of Zn ranging from 2% to 8%. Every 10 minutes, a new connection was made to a different sample, and then its connection with the first strip was broken. This procedure made it possible to cycle

through all Ni/Zn samples in a single test. Arrows indicate each sample switch in Figure 1. Finally, after about 115 minutes of recording current and potential data, the Polyfibroblast strip was completely disconnected from the steel, leaving the metal without CP. At this point, the CP current dropped to zero causing the electrochemical potential of the steel to shift more positive values (Fig. 1 A). In the absence of CP, the steel started corroding, and the corrosion products started staining the surface of steel.

The data shown in Figure 1 is preliminary. The negative shift in the electrical potential in Figure 1 B indicates the capability of Polyfibroblast to provide CP to steel. A -100 mV polarization typically indicates effective cathodic protection. However, the results at this stage do not indicate a significant correlation with zinc concentration. Additional work is necessary to quantify the degree of cathodic protection offered by the Polyfibroblast containing different amounts of zinc.

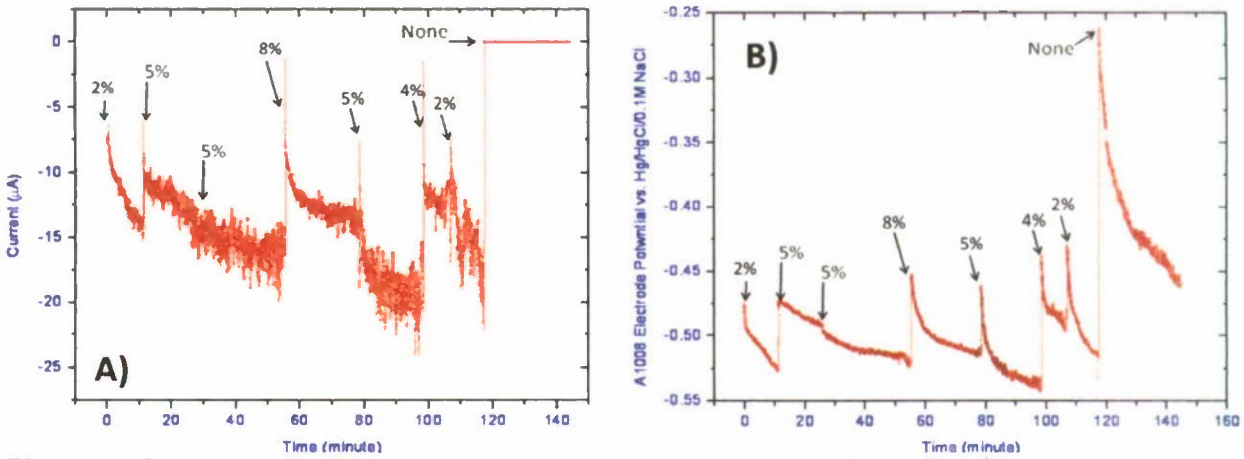

Figure 1: *Cathodic protection data for A1008 shorted to polyurethane-Polyfibroblast strip containing different alloy concentrations of Zn noted by weight %: A.) CP current due to shorting the Zn-containing Polyfibroblast to steel; B.) Negative shift in the electrochemical potential of the steel shorted to Zn-containing Polyfibroblast. A -100-mV polarization indicates effective cathodic protection.*

3.2 ICP and EDS analysis

ICP and EDS analysis have been performed to evaluate the concentration of Ni, Zn, and P in the electroless alloys. These measurements serve as a check against x-ray photoelectron spectroscopy (XPS) measurements performed over a year ago. The data in Figure 2 show that the previous data overestimated the amount of zinc by nearly a factor of two. More importantly, it shows that the basic plating bath tends to deposit more zinc than does the acidic version of the plating bath.

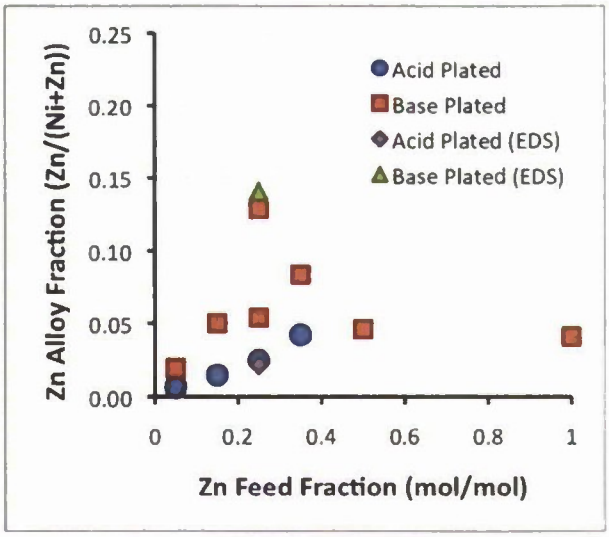

Figure 2: *Plot of Zn feed fraction in the plating bath versus the measured value in the electroless alloy. Up to 35% Zn in the plating bath, the amount of zinc plated is approximately 1/3 of the feed ratio.*

3.3 Plating Bath pH

New experiments have revealed that alkaline plating baths etch the polymer skin layer. Fresh microcapsules placed in plating baths with a pH of 4.7, 10, and 12.4 are compared in Figure 3. While the control samples and acid bath samples remain transparent, the basic plating baths both resulted in opaque microcapsules after only 1 hour. The opaque appearance results from spherical polymer precipitates that form by internal polymerization. The internal polymerization suggests that the basic solution etches the polymer skin layer, allows water to infiltrate the microcapsule, and then drives unwanted internal curing.

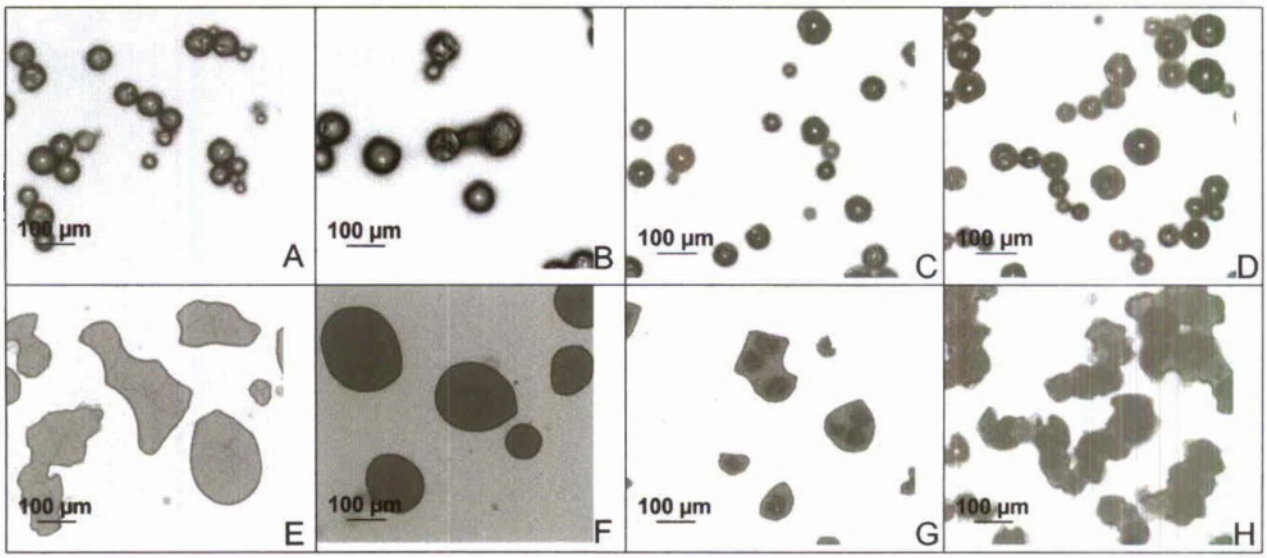

Figure 3: *Optical micrographs of microcapsules exposed to plating baths for 1 hour. A) Control with no plating bath exposure, B) pH 4.7, C) pH 10, D) pH 12.4. E-H) same as above but after squashing with a cover slip to reveal internal curing.*

Under normal circumstances, a protective metal coating deposits rapidly during the plating process. However, it is interesting to note that significant etching of the polymer skin layer may be a competing reaction. This result also confirms our previous qualitative experience that acidic plating baths yield higher quality microcapsules. But as Figure 1 shows, the acidic plating baths do not deposit as much zinc from the plating bath.

3.4 Polymer Formulation Advances

While most work continues on a formulation containing 85% isophorone diisocyanate, ongoing efforts are looking at alternative monomers with potentially superior barrier properties. One such monomer is hexamethylene diisocyanate (HMDI). Consisting mostly of aliphatic carbons, HMDI forms a polymer with a similar structure to Nylon 6. Nylon 6 is well known for its toughness and wear resistance, characteristics that are highly sought after in coatings. Preliminary experiments with polymerized HMDI in our lab support this favorable comparison.

This month we were finally able to synthesize microcapsules containing HMDI. The synthesis was more challenging than expected due to its unusually low viscosity. The lower viscosity caused an unacceptably fast rate of droplet breakup and coalescence. In the presence of crosslinker, this rapid evolution of the droplets caused uncontrolled polymerization. Only by adding HMDI prepolymer was it possible to synthesize microcapsules in high yield.

3.5 Spray Painting

PPG has successfully spray painted several test panels using 25 μm Polyfibroblast microcapsules. Early indications on an optical microscope showed that ample resin remained within the microcapsules even after spraying and drying. Although no obvious evidence suggested premature rupture of the microcapsules, future inspections will be performed using a fluorescent microscope. Background fluorescence from the Nile Red in the resin matrix will serve to indicate premature rupture. Previous experiments performed on gravity-fed coatings of Polyfibroblast showed no evidence of fluorescence in the matrix.

3.6 Batch Size

PPG has successfully increased its batch size up to 120 g. The particle mean diameter is 25.2μm, which is slightly larger than the value of 16.1 μm measured for a 20 g batch under the same conditions (Fig. 4). Interestingly, the polydispersity decreased slightly from 0.387 to 0.366.

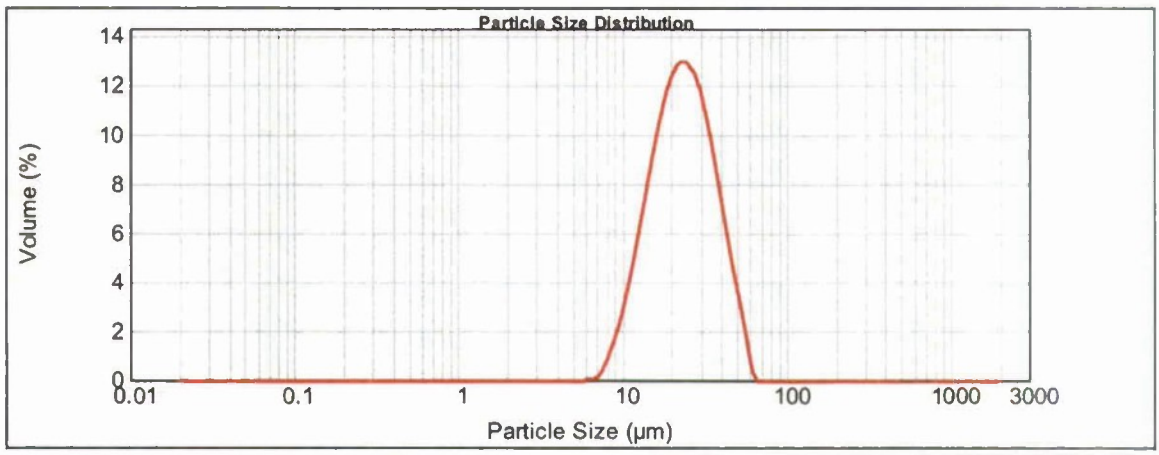

Figure 4: *Particle size distribution for 120 g batch of microcapsules.*

3.7 Solvent Stability

Since Polyfibroblast will most likely be stored in an oil-based paint, the microcapsules must have high solvent resistance. The first tests show that no significant amount of liquid resin is removed by soaking in a number of solvents for two hours. Note how the solvent soaked samples have roughly the same quantity of liquid as the control (Fig. 5).

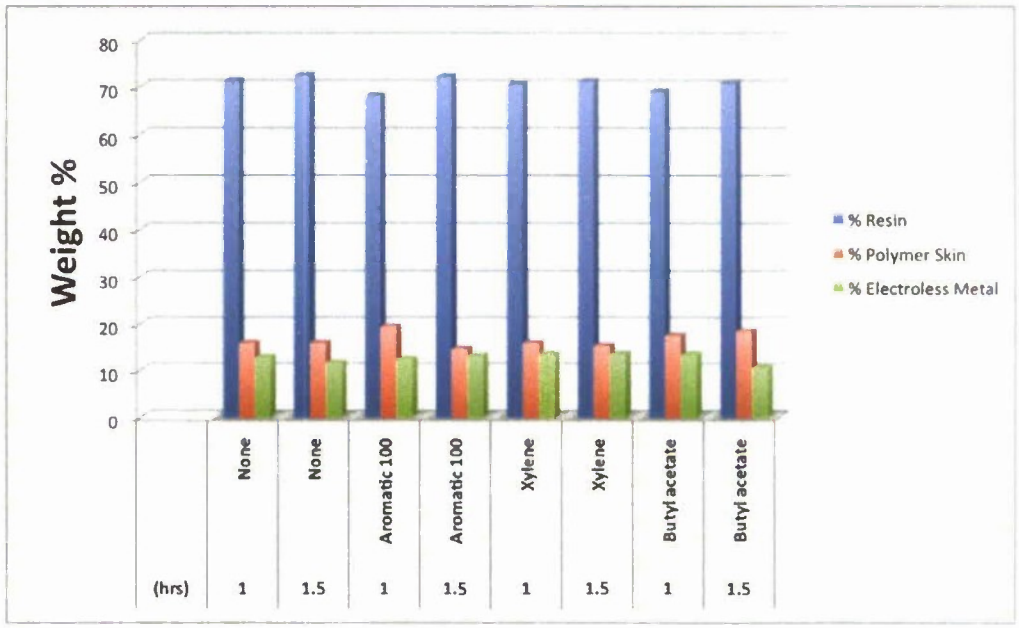

Figure 5: *Thermogravimetric Analysis (TGA) data showing the weight percent of liquid resin, polymer skin, and electroless metal as a function of solvent exposure. No significant loss of resin appears to have occurred within the uncertainty of the measurement.*

4 Next Steps

4.1 PPG: Processing

PPG will continue to evaluate the sprayability of the Polyfibroblast filler. They will inspect spray painted samples with a fluorescence microscope to determine whether premature microcapsule rupture occurred during the spraying process. They will also spray paint samples with other resins besides MIL-P-26915. Once the sprayed coatings can be qualified under a military specification such as the one for MIL-P-26916, their properties will be compared using ASTM standards for adhesion, hardness, wear, moisture resistance, QUV testing, and accelerated weathering (salt spray).

Development will also begin on a process that eliminates the current freeze-drying step. Due to the large amounts of energy required and the limited size of most lyophilizers, the current method is prohibitively expensive. The most promising current alternative is to displace water with a low boiling point, low surface tension solvent such as isopropanol and allow it to air dry, possibly under agitation.

In order to facilitate the synthesis of larger batches in more rapid succession, PPG will also investigate whether the emulsion can be removed from a rotor-stator mixer after a few minutes for polymer skin formation and then transferred to a low-speed mixer for subsequent polymer skin growth without affecting the particle size distribution.

4.2 APL: Performance

Due to the difficulty of encapsulating surfactant, APL will also explore alternative methods, such as adding silane adhesion promoters or oils that can produce similar improvements in adhesion. Although these alternatives do not help with foaming expansion during cure, they may actually act to improve the tenacity of the polymer scar by improving the adhesion with the underlying steel.

Additionally, we will continue to perform electrochemical measurements to verify the preliminary findings presented in this report.